

USE OF YTTRIUM, ZIRKONIUM, LANTHANUM, CERIUM, PRASEODYMIUM AND/OR NEODYMIUM AS
REINFORCING AGENT FOR AN ANTICORROSIN COATING COMPOSITION

The present invention sets out to develop an anticorrosion coating for metal parts, preferably free of hexavalent chromium, that has improved anticorrosion properties.

5 The present invention applies to all types of metal parts, in particular in steel or cast iron or whose surface is formed of a layer of zinc or zinc alloy, which require high resistance to corrosion, on account of their intended use in the automotive industry for example. Anticorrosion coating compositions, free of hexavalent chromium, have already been recommended. Some of these compositions contain a particulate metal. The particulate metal, such as zinc and/or aluminium, is in
10 suspension in the composition and provides the metal part with sacrificial protection against a corrosive medium. Aqueous anticorrosion coating compositions for example have been described for metal parts, containing a particulate metal, an appropriate solvent, a thickener and a binder formed of a silane. Particulate metal-based compositions have also been described whose storage stability and
15 anticorrosion performance are improved through the incorporation of molybdenum oxide (MoO_3) in the composition.

Within the scope of the present invention, the applicant has discovered that it is possible to improve the anticorrosion properties of compositions containing particulate metal by incorporating therein at least one element chosen from among
20 yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium, in the form of oxides or salts.

The anticorrosion performance of coating compositions containing particulate metal prove to be further improved when the above-cited elements are associated with molybdenum oxide.

25 The compositions containing particulate metal concerned by the present invention may be aqueous phase or organic phase compositions. They are recommended when high resistance to corrosion is required.

The subject of the present invention is therefore the use of at least one element chosen from among yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium in the form of oxides or salts, as agent to reinforce the anticorrosion properties of an anticorrosion coating composition containing a particulate metal, in aqueous or organic phase, for metal parts.

A further subject of the invention is the use of at least one of the above-cited elements, optionally associated with molybdenum oxide MoO_3 , as reinforcing agent for the anticorrosion properties of an anticorrosion coating composition containing a particulate metal, in aqueous or organic phase, for metal parts.

Without this interpretation being restrictive, it would seem that the presence of at least one of the above-cited elements makes it possible to reinforce the efficacy of the anticorrosion protection imparted by the particulate metal in the composition.

The particulate metal present in the composition is preferably added in powder form, of different geometric, homogeneous or heterogeneous structures, in particular spherical, laminar, lenticular forms or other specific forms.

The oxides or salts of the above-cited elements which are used as reinforcing agents for the anticorrosion properties of the composition, are generally in powder form whose particles have a D_{50} of less than $20\text{ }\mu\text{m}$ (the value D_{50} means that 50% by number of the particles have a particle size of less than this value, and 50% by number of the particles have a particle size greater than this value). During the preparation of the coating composition, a prior particle grinding or dispersion step (to break up agglomerates into elementary particles) may be conducted so that the composition contains particles with a D_{50} of less than $3\text{ }\mu\text{m}$.

These oxides or salts may be fully soluble, partially soluble or completely insoluble in aqueous phase or organic phase. They may be in dispersed or solubilised form within the composition.

Yttrium salts are advantageously chosen from among yttrium acetate, chloride, formate, carbonate, sulfamate, lactate, nitrate, oxalate, sulfate, phosphate and aluminate ($\text{Y}_3\text{Al}_5\text{O}_{12}$), and their mixtures.

Yttrium oxide is advantageously in the form Y_2O_3 .

Yttrium is preferably used in oxide form.

The yttrium oxide Y_2O_3 used to prepare the coating composition is generally in the form of particles having a size of between 1 μm and 40 μm , with a D_{50} of approximately 6 to 8 μm . When preparing the coating composition, a prior particle grinding or dispersion step (to break up agglomerates into elementary particles) may be conducted so that the composition contains particles having a D_{50} of less than 3 μm .

Zirconium salts are preferably chosen from among zirconium carbonate, silicate, sulfate, and titanate, and their mixtures.

Zirconium oxide is advantageously in the form ZrO_2 .

Lanthanum salts are advantageously chosen from among lanthanum acetate, oxalate, nitrate, sulfate, carbonate, phosphate and aluminate ($LaAlO_3$), and their mixtures.

Lanthanum oxide is preferably in the form La_2O_3 .

Cerium salts are advantageously chosen from among cerium chloride, carbonate, acetate, nitrate, oxalate, sulfate, phosphate, molybdate ($Ce_2(MoO_4)_3$) and tungstate ($Ce_2(WO_4)_3$), and their mixtures.

Cerium oxide is advantageously in the form CeO_2 .

Cerium is preferably used in the form of cerium chloride or CeO_2 .

Praseodymium salts are advantageously chosen from among praseodymium carbonate, chloride, nitrate, oxalate and sulfate, and their mixtures.

Praseodymium oxide is advantageously in the form Pr_6O_{11} .

Neodymium salts are advantageously chosen from among neodymium carbonate, chloride, nitrate and sulfate, and their mixtures.

Neodymium oxide is advantageously in the form Nd_2O_3 .

When the composition also contains molybdenum oxide MoO_3 associated with one of the above-cited elements used as reinforcing agent for the anticorrosion properties of the composition, MoO_3 is advantageously incorporated in essentially pure orthorhombic crystalline form, having a molybdenum content of more than around 60 % by weight.

Preferably, the molybdenum oxide MoO_3 is in the form of particles having a size of between 1 μm and 200 μm .

Preferably, said reinforcing agent for the anticorrosion properties of the composition is associated with molybdenum oxide MoO_3 in a weight ratio of $0.25 < \text{anticorrosion property reinforcing agent} : \text{MoO}_3 < 20$, preferably $0.5 < \text{anticorrosion property reinforcing agent} : \text{MoO}_3 < 16$, further preferably $0.5 < \text{anticorrosion property reinforcing agent} : \text{MoO}_3 < 14$.

Preferably yttrium oxide Y_2O_3 is used in association with molybdenum oxide MoO_3 . A further subject of the invention is the use of yttrium oxide Y_2O_3 in association with molybdenum oxide MoO_3 in a weight ratio of $0.25 < \text{Y}_2\text{O}_3 : \text{MoO}_3 < 20$, preferably $0.5 < \text{Y}_2\text{O}_3 : \text{MoO}_3 < 16$, further preferably $0.5 < \text{Y}_2\text{O}_3 : \text{MoO}_3 < 14$.

A further subject of the invention concerns anticorrosion coating compositions for metal parts, comprising:

- at least one particulate metal;
- a reinforcing agent for the anticorrosion properties of the composition, chosen from among yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium, in the form of oxides or salts, optionally associated with molybdenum oxide MoO_3 ;
- a binder; and
- either water, optionally associated with one or more organic solvents, or one or more organic solvents miscible *inter se*.

The coating composition contains at least one particulate metal, i.e. one or more particulate metals.

Advantageously, the particulate metal content lies between 10 % and 40 % by weight relative to the weight of the composition.

The particulate metal may be chosen from among zinc, aluminium, tin, manganese, nickel, their alloys, and their mixtures.

Preferably the particulate metal is chosen from among zinc, aluminium, their alloys and their mixtures. Preferably the alloys are chosen from the alloys of zinc and aluminium containing at least 3 % by weight aluminium, preferably 7 % by weight of aluminium, and the zinc and tin alloys containing at least 10 % by weight of tin.

The content of anticorrosion property reinforcing agent of the composition preferably lies between 0.5 % and 10 % by weight relative to the weight of the composition, preferably between 1 % and 8 % by weight relative to the weight of the

composition, further preferably between 1 % and 7 % by weight relative to the weight of the composition.

The reinforcing agent for the anticorrosion properties of the composition is advantageously yttrium, preferably in the oxide form Y_2O_3 , or cerium preferably in the form of cerium chloride.

The reinforcing agent for the anticorrosion properties of the composition is advantageously associated with molybdenum oxide MoO_3 in a weight ratio of $0.25 < \text{anticorrosion property reinforcing agent} : MoO_3 < 20$, preferably $0.5 < \text{anticorrosion property reinforcing agent} : MoO_3 < 16$, further preferably $0.5 < \text{anticorrosion property reinforcing agent} : MoO_3 < 14$.

The binder content preferably lies between 3 % and 20 % by weight relative to the weight of the composition. The binder may be of organic and/or mineral type in aqueous or organic phase. The choice of the binder depends on different criteria, among which is the baking temperature of the coating composition.

The binder is preferably chosen from among an alcoxylated silane, optionally organofunctionalised, such as γ -glycidoxypropyltrimethoxysilane or γ -glycidoxypropyltrimethoxysilane, a silicone resin, a silicate of sodium and/or potassium and/or lithium, a zirconate, a titanate, an epoxy resin, a phenoxy resin, an acrylic and their mixtures.

The binder may be associated with a crosslinking agent of phenolic type, aminoplast type, or dicyandiamide type. Acid catalysts may also be added in order to catalyse the crosslinking reaction.

If the composition is in aqueous phase, a colloidal silica may be used in association with resins, as binder.

If the coating composition is in aqueous phase, the liquid phase is formed of water and may also contain up to 30 % by weight of an organic solvent or a mixture of organic water-miscible solvents.

If the coating composition is in organic phase, the liquid phase is entirely made up of an organic solvent or a mixture of organic solvents miscible *inter se*.

The organic solvent or solvents are chosen in relation to the binder, so as to solubilise the latter or stabilise a dispersion thereof. The organic solvent or solvents are advantageously chosen from white spirit, alcohols, ketones, aromatic solvents

and glycol solvents such as glycol ethers, in particular diethyleneglycol, triethyleneglycol and dipropyleneglycol, acetates, polyethyleneglycol and nitropropane, and their mixtures.

5 The coating composition may also contain a thickener if the type of application so requires, if it is to be applied by dipping-centrifuging for example.

The content of thickening agent is advantageously less than 7 % by weight relative to the weight of the composition, preferably between 0.005 % and 7 % by weight relative to the weight of the composition.

10 The thickening agent is advantageously chosen from among the cellulose derivatives such as hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose or hydroxypropylmethylcellulose, xanthane gum, associative thickeners of polyurethane or acrylic type, silicas, silicates such as silicates of magnesium and/or lithium optionally treated, or organophilic clays, and their mixtures.

15 The coating composition may also comprise a lubricating agent in sufficient quantity to obtain a self-lubricated system, chosen in particular from among polyethylene, polytetrafluoroethylene, MoS₂, graphite, polysulfones, synthetic or natural waxes and nitrides, and their mixtures.

20 If it is in aqueous phase, the coating composition may also contain other additives compatible with the binder, chosen from among an anti-foam agent such as Schwego foam (emulsified hydrocarbon) from Schwegman, a wetting agent such as an ethoxylated monylphenol or an ethoxylated polyalcohol, a surfactant agent such as Aerosol TR 70 (sodium sulfosuccinate) from Cytec, and a biocide such as Ecocide D₇₅ from Progiva, and a weak acid such as boric acid to adjust the pH of the
25 composition.

In preferred manner, the coating composition contains the following ingredients:

- 10 % to 40 % by weight of at least one particulate metal;
- 0.5 % to 10 % by weight of an anticorrosion property reinforcing agent for the
30 composition chosen from yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium, in the form of oxides or salts, optionally associated with molybdenum oxide MoO₃;

- up to 7 % by weight of a thickener;
- 3 % to 20 % by weight of a binder;
- up to 3 % by weight, preferably 0.05 % to 2 % by weight of a sodium and/or potassium and/or lithium silicate;
- 5 - up to 7 % by weight of one or more lubricating agents;
- 1 % to 30 % by weight of an organic solvent or a mixture of organic solvents;
- optionally 0.1 % to 10 % by weight of a weak mineral acid such as boric acid;
- optionally 0.01 % to 1 % by weight of an anionic surfactant; and
- water to make up to 100 %.

10 If the above-cited anticorrosion property reinforcing agent is associated with molybdenum oxide, the latter preferably represents 0.5 % to 2 % by weight of the composition.

Evidently, the present invention also extends to anticorrosion coatings applied to metal parts using the above-cited compositions.

15 Application may be made by spraying, dipping-draining or dipping-centrifuging, the layer of coating then being subjected to a baking operation (by convection or infrared for example) preferably conducted at a temperature of between 70°C and 350°C, for approximately 10 to 60 minutes, by convection.

20 According to one advantageous embodiment, the anticorrosion coating derives from an application operation involving, prior to the baking operation, a drying operation of the coated metal parts (by convection, or infrared for example), in particular by convection at a temperature in the region of 70°C for approximately 10 to 30 minutes on line.

25 Under these conditions, the thickness of the dry film so applied lies between 3 μm (11 g/m^2) and 15 μm (55 g/m^2), preferably between 4 μm (15 g/m^2) and 10 μm (40 g/m^2), further preferably between 5 μm (18 g/m^2) and 10 μm (40 g/m^2).

The present invention also extends to the metal substrate, preferably in steel, provided with an anticorrosion coating applied using the above-cited compositions.

30 This itself may be coated with another coating to further reinforce some properties, such as anticorrosion protection or lubrication. A coating to reinforce the anticorrosion protection may contain an alkaline silicate, in particular a sodium

and/or potassium and/or lithium silicate, an acrylic, a zirconate, a titanate, a silane, an epoxy resin, a phenol resin or one of their mixtures, these resins optionally being associated with a colloidal silica. A coating for lubrication may contain a lubricating agent chosen from among polyethylene, polytetrafluoroethylene, MoS₂, graphite, polysulfones, synthetic or natural waxes, and nitrides, and their mixtures.

Corrosion tests

A) Influence of yttrium oxide (Y₂O₃), in aqueous phase, optionally associated with molybdenum oxide (MoO₃) on anticorrosion performance.

Comparative experiments were conducted on the coating compositions given in table 1.

Table 1

weight %	composition			
	1	2	3	4
Y ₂ O ₃ ¹	0	3.0	0	3.0
MoO ₃	0	0	0.9	0.9
Zinc ²	23.6			
Aluminium ³	3.0			
Silane A187 ⁴	10.1			
Sodium silicate 20N32 ⁵	0.9			
Rempcopal® N4 100 ⁶	1.4			
Rempcopal® N9 100 ⁷	1.6			
Dipropylene glycol	7.5			
Aerosil® 380 ⁸	<0.1			
Schwego Foam® 8325 ⁹	0.5			
Boric acid	0.8			
Deionised water	Up to 100 %			

¹ Y₂O₃ of 99.99 % purity (Rhodia)

² Zinc in paste form, approx. 92 % in white spirit (80 % Alu Stapa PG Chromal VIII, from Eckart Werke)

³ Aluminium, approx. 80 % in dipropylene glycol

⁴ γ -glycidoxypolytrimethoxysilane (Crompton)

⁵ Sodium silicate (Rhodia)

⁶ Wetting agent of ethoxylated nonylphenol type (Uniqema)

5 ⁷ Wetting agent of ethoxylated nonylphenol type (Uniqema)

⁸ Anti-sedimentation agent of silica type (Degussa)

⁹ Antifoam of hydrocarbon type.

Prepared samples

- Treated substrate: degreased, shot-blasted steel screws
- 10 - Application of coating composition: dip-centrifuging
- Baking: 25 min at 310°C
- Weight of coating layer: $26 \pm 2 \text{ g/m}^2$

The steel screws treated in this manner were tested with salt spray according to standard NFISO 9227. Results of salt spray resistance are given in table 2.

15

Table 2

Composition	Y ₂ O ₃ (weight %)	MoO ₃ (weight %)	Resistance to salt spray (N° hours)
1	0	0	140-260
2	3	0	840
3	0	0.9	500
4	3	0.9	1300

Table 2 clearly shows that the addition of yttrium oxide Y₂O₃ to coating compositions increases resistance to salt spray in samples treated with these compositions.

20

Also, when yttrium oxide Y₂O₃ is associated with molybdenum oxide MoO₃, the anticorrosion performance is further improved. An interaction is observed or a synergy effect between Y₂O₃ and MoO₃, which increases the composition's anticorrosion performance.

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B) Influence of zinc alloyed with 7 % aluminium (Stapa Zn₄Al₇, from Eckkart Werke) on anticorrosion performance.

Comparative experiments were conducted on the coating compositions listed in table 3.

Table 3

composition	
5	Identical to composition n° 3
6	Identical to composition n° 4
7	Identical to composition n°4 with the difference that 30 % by weight zinc is replaced by zinc alloyed with 7 % by weight of aluminium (Stapa Zn ₄ Al ₇ , from Eckart Werke).

Prepared samples:

- treated substrate: degreased, shot-blasted steel screws
- Application of coating composition: dip-centrifuging
- Baking: 25 min at 310°C
- Weight of coating layer: $26 \pm 2 \text{ g/m}^2$

The steel screws were treated with the coating compositions in table 3, then tested with salt spray according to standard NFISO 9227.

Results of resistance to salt spray are given in table 4.

Table 4

Composition	Y ₂ O ₃ (weight %)	MoO ₃ (weight %)	Stapa Zn ₄ Al ₇ /Zn (weight %)	Resistance to salt spray (N° hours)
5	0	0.9	0	450
6	3	0.9	0	1370
7	3	0.9	30	1900

Table 4 shows that the anticorrosion performance of the composition is better with alloyed zinc than with zinc.

C) Influence of cerium chloride in aqueous phase on anticorrosion performance

Comparative experiments were conducted on the coating compositions listed in table 5.

Table 5

Composition	
8	Identical to composition n° 3
9	Identical to composition n° 1 with the difference that 0.5 % by weight of cerium chloride is added in addition to the other ingredients
10	Identical to composition n°1 with the difference that 2 % by weight of cerium chloride is added in addition to the other ingredients

Prepared samples

- Treated substrate: degreased, shot blasted steel screws
- Application of coating composition: dip-centrifuging
- Baking: 25 min at 310°C
- Weight of coating layer: $26 \pm 2 \text{ g/m}^2$

The steel screws were treated with the coating compositions in table 5, then tested with salt spray in accordance with standard NFISO 9227.

The results of resistance to salt spray are given in table 6.

Table 6

composition	Cerium chloride (weight %)	Resistance to salt spray (N° hours)
8	0	200
9	0.5	500
10	2	770

Table 6 clearly shows that the addition of cerium chloride to coating compositions increases the resistance to salt spray of the samples treated with these compositions.

D) Influence of yttrium carbonate in aqueous phase on anticorrosion performance

Comparative experiments were conducted on the coating compositions listed in table 7.

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Table 7

Composition	
11	Identical to composition n° 1
12	Identical to composition n° 3 with the difference that 0.8 % by weight of MoO_3 is present in the composition instead of 0.9 %
13	Identical to composition n° 2 with the difference that 3 % by weight of Y_2O_3 are replaced with 6.9 % by weight of yttrium carbonate
14	Identical to composition n° 4 with the difference that 3 % by weight of Y_2O_3 are replaced with 6.9 % by weight of yttrium carbonate and 0.8 % by weight of MoO_3 are present in the composition instead of 0.9 %

Steel screws were prepared, treated and tested as in example 1. Results of salt spray resistance are given in table 8.

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Table 8

composition	Yttrium carbonate (weight%)	MoO_3 (weight %)	Resistance to salt spray (N° hours)
11	0	0	288
12	0	0.8	400
13	6.9	0	288
14	6.9	0.8	1296

Table 8 clearly shows that, when yttrium carbonate is associated with molybdenum oxide MoO_3 , the anticorrosion performance is improved. An interaction is observed or a synergy effect between yttrium carbonate and MoO_3 , which increases the composition's anticorrosion performance.

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E) Influence of various oxides in aqueous phase on anticorrosion performance

Comparative experiments were conducted on the coating compositions listed in table 9.

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Table 9

Composition	
15	Identical to composition n° 1
16	Identical to composition n° 3
17	Identical to composition n° 2
18	Identical to composition n° 4
19	Identical to composition n° 2 with the difference that Y_2O_3 is provided by Sogemet
20	Identical to composition n° 4 with the difference that Y_2O_3 is provided by Sogemet
21	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with CeO_2 provided by Rhodia
22	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with CeO_2 provided by Rhodia
23	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with CeO_2 provided by Sogemet
24	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with CeO_2 provided by Sogemet
25	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with La_2O_3 provided by Rhodia
26	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with La_2O_3 provided by Rhodia
27	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with La_2O_3 provided by Sogemet
28	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with La_2O_3 provided by Sogemet

29	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with Pr_6O_{11}
30	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with Pr_6O_{11}
31	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with Nd_2O_3
32	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with Nd_2O_3
33	Identical to composition n° 2 with the difference that Y_2O_3 is replaced with ZrO_2
34	Identical to composition n° 4 with the difference that Y_2O_3 is replaced with ZrO_2

E-1) Electrochemistry

- Treated substrates : degreased and sanded steel plates,
- 5 - Application of coating composition : by means of a hand-coater,
- Baking : 25 min at 310°C,
- Weight of coating layer : 26 ± 2 g/m².

10 Polarisation resistance of the coatings was measured during one hour with SOLARTRON 1250 analyzer (Schlumberger), air exposed, with a scanning rate of ± 10 mV at 0.1 mV.s^{-1} . Results of these measurements are given in table 10. The higher the value of polarization resistance, the better the anticorrosion performance of the coatings is expected.

15

Table 10

composition	Oxide	Oxide (weight%)	MoO ₃ (weight %)	Polarisation Resistance ($\Omega \cdot \text{cm}^2$)
15	-	0	0	3300
16	-	0	0.9	9100
17	Y ₂ O ₃ Rhodia	3	0	n.d.
18	Y ₂ O ₃ Rhodia	3	0.9	12100

21	CeO ₂ Rhodia	3	0	10600
22	CeO ₂ Rhodia	3	0.9	12000
23	CeO ₂ Sogemet	3	0	10000
24	CeO ₂ Sogemet	3	0.9	12000
25	La ₂ O ₃ Rhodia	3	0	n.d.
26	La ₂ O ₃ Rhodia	3	0.9	11900
27	La ₂ O ₃ Sogemet	3	0	9300
28	La ₂ O ₃ Sogemet	3	0.9	10100
29	Pr ₆ O ₁₁	3	0	9900
30	Pr ₆ O ₁₁	3	0.9	9800
31	Nd ₂ O ₃	3	0	9400
32	Nd ₂ O ₃	3	0.9	10000
33	ZrO ₂	3	0	9200
34	ZrO ₂	3	0.9	12000

Table 10 clearly shows that the addition of oxide of yttrium, cerium, lanthanum, praseodymium, neodymium or zirconium to coating compositions increases the polarization resistance of coatings, which indicates that the corrosion resistance of the coatings will be likely increased.

E-2) Corrosion resistance

Steel screws were prepared, treated and tested as in example 1. Results of salt spray resistance are given in table 11.

Table 11

Composition	Oxide	Oxide (weight%)	MoO ₃ (weight %)	Resistance to salt spray (N° hours)
15	-	0	0	288
16	-	0	0.9	400
17	Y ₂ O ₃ Rhodia	3	0	1056
18	Y ₂ O ₃ Rhodia	3	0.9	>1500

19	Y ₂ O ₃ Sogemet	3	0	1296
20	Y ₂ O ₃ Sogemet	3	0.9	>1656
21	CeO ₂ Rhodia	3	0	144
22	CeO ₂ Rhodia	3	0.9	720
23	CeO ₂ Sogemet	3	0	144
24	CeO ₂ Sogemet	3	0.9	792
25	La ₂ O ₃ Rhodia	3	0	336
26	La ₂ O ₃ Rhodia	3	0.9	552
27	La ₂ O ₃ Sogemet	3	0	552
28	La ₂ O ₃ Sogemet	3	0.9	864
29	Pr ₆ O ₁₁	3	0	504
30	Pr ₆ O ₁₁	3	0.9	864
31	Nd ₂ O ₃	3	0	288
32	Nd ₂ O ₃	3	0.9	1560
33	ZrO ₂	3	0	288
34	ZrO ₂	3	0.9	456

Table 11 clearly shows that the addition of oxide of yttrium, lanthanum, praseodymium, neodymium or zirconium to coating compositions increases the resistance to salt spray of the samples treated with these compositions. The best oxide appears to be Y₂O₃, but Neodymium, Praseodymium and Lanthanum give also very good results too.

Furthermore, when the oxide is associated with molybdenum oxide MoO₃, the anticorrosion performance is further improved. An interaction is observed or a synergy effect between the oxide and MoO₃, which increases the composition's anticorrosion performance.

CLAIMS

1. Use of at least one element chosen from among yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium, in the form of oxides or salts, as reinforcing agent for the anticorrosion properties of a coating composition containing a particulate metal, in aqueous or organic phase, for metal parts.

5 2. Use according to claim 1, characterized in that one of the above-cited elements as anticorrosion property reinforcing agent is associated with molybdenum oxide MoO_3 .

3. Use according to any of claims 1 or 2, to reinforce the efficacy of the anticorrosion protection imparted by the particulate metal, the latter preferably being
10 added to the composition in powder form of varying geometric structure, homogenous or heterogeneous, in particular of spherical, lamellar or lenticular structure.

4. Use according to any of claims 1 to 3, characterized in that the element used is yttrium, preferably in the oxide form Y_2O_3 , or in the form of yttrium
15 carbonate.

5. Use according to claim 4, characterized in that yttrium oxide Y_2O_3 is used in the form of particles having a size of between 1 μm and 40 μm with a D_{50} of less than 3 μm .

6. Use according to any of claims 1 to 3, characterized in that the
20 element used is cerium, preferably in the form of cerium chloride or in the oxide form CeO_2 .

7. Use according to any of claims 1 to 3, characterized in that the element used is La_2O_3 , Pr_6O_{11} , Nd_2O_3 or ZrO_2 .

8. Use according to any of claims 2 to 7, characterized in that
25 molybdenum oxide MoO_3 is used in an essentially pure orthorhombic crystalline form having a molybdenum content greater than approximately 60 % by weight.

9. Use according to any of claims 2 to 8, characterized in that the molybdenum oxide MoO_3 is in the form of particles having a size of between 1 μm and 200 μm .

10. Use according to any of claims 2 to 9, characterized in that said anticorrosion property reinforcing agent is associated with molybdenum oxide MoO_3 in a weight proportion of $0.25 < \text{anticorrosion property reinforcing agent} : \text{MoO}_3 < 20$, preferably $0.5 < \text{anticorrosion property reinforcing agent} : \text{MoO}_3 < 16$, further preferably $0.5 < \text{anticorrosion property reinforcing agent} : \text{MoO}_3 < 14$.

11. Anticorrosion coating composition for metal parts, characterized in that it contains:

- at least one particulate metal;
- a reinforcing agent for the anticorrosion properties of the composition chosen from among yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium, in the form of oxides or salts;
- a binder; and
- either water optionally associated with one or more organic solvents, or one or more inter-miscible organic solvents,

12. Composition according to claim 11, characterized in that the reinforcing agent for the anticorrosion properties of the composition is associated with molybdenum oxide MoO_3 .

13. Composition according to claim 12, characterized in that it contains 0.5 % to 2 % by weight molybdenum oxide MoO_3 .

14. Composition according to any of claims 11 to 13, characterized in that it contains 10 % to 40 % by weight of at least one particulate metal.

15. Composition according to any of claims 11 to 14, characterized in that the particulate metal is chosen from among zinc, aluminium, tin, manganese, nickel, their alloys, and their mixtures.

16. Composition according to any of claims 11 to 15, characterized in that the particulate metal is chosen from among zinc, aluminium, their alloys and their mixtures.

17. Composition according to any of claims 11 to 16, characterized in that it contains 0.5 % to 10 % by weight of said reinforcing agent for the anticorrosion properties of the composition, preferably from 1 % to 8 % by weight, further preferably from 1 to 7 % by weight, relative to the weight of the composition.

18. Composition according to any of claims 11 to 17, characterized in that the reinforcing agent for the anticorrosion properties of the composition is yttrium, preferably in the oxide form Y_2O_3 or in the form of yttrium carbonate.

19. Composition according to any of claims 11 to 18, characterized in that the reinforcing agent for the anticorrosion properties of the composition is cerium, preferably in the form of cerium chloride or in the oxide form CeO_2 .

20. Composition according to any of claims 11 to 18, characterized in that the reinforcing agent for the anticorrosion properties of the composition is chosen among La_2O_3 , Pr_6O_{11} , Nd_2O_3 and ZrO_2 .

21. Composition according to any of claims 11 to 19, characterized in that said reinforcing agent for the anticorrosion properties of the composition is associated with molybdenum oxide MoO_3 in a weight proportion $0.25 < \text{anticorrosion property reinforcing agent : } MoO_3 < 20$, preferably $0.5 < \text{anticorrosion property reinforcing agent : } MoO_3 < 16$, further preferably $0.5 < \text{anticorrosion property reinforcing agent : } MoO_3 < 14$.

22. Composition according to any of claims 11 to 21, characterized in that it contains 3 % to 20 % by weight of an organic binder and/or mineral binder, in aqueous or organic phase.

23. Composition according to any of claims 11 to 22, characterized in that the binder is chosen from among an alcoxylated silane, optionally organofunctionalised, a silicone resin, a colloidal silica, a silicate of sodium and/or potassium and/or lithium, a zirconate, a titanate, an epoxy resin, a phenoxy resin, an acrylic and their mixtures, optionally associated with a crosslinking agent of phenolic type, aminoplast type, or dicyandiamide type, or with an acid catalyst.

24. Composition according to claim 23, characterized in that the binder is an organo-functionalised silane such as γ -glycidoxypyrpyl-trimethoxysilane and γ -glycidoxypyrpyltriethoxysilane.

25. Composition according to any of claims 11 to 24, characterized in that it contains an organic solvent chosen from among white spirit, alcohols, ketones, aromatic solvents and glycol solvents such as glycol ethers, in particular diethyleneglycol, triethyleneglycol and dipropyleneglycol, acetates, polyethyleneglycol and nitropropane, and their mixtures.

26. Composition according to any of claims 11 to 25, characterized in that it also contains up to 7 % by weight of a thickening agent.

27. Composition according to any of claims 11 to 26, characterized in that the thickening agent is chosen from among cellulose derivatives such as hydroxymethyl-cellulose, hydroxyethylcellulose, hydroxypropylcellulose or hydroxypropylmethylcellulose, xanthane gum, associative thickeners of polyurethane or acrylic type, silicas, silicates such as silicates of magnesium and/or lithium optionally treated, or organophilic clays, and their mixtures.

28. Composition according to any of claims 11 to 27, characterized in that it also contains a lubricating agent to obtain a self-lubricated system chosen from among polyethylene, polytetrafluoroethylene, MoS₂, graphite, polysulfones, synthetic or natural waxes and nitrides, and their mixtures.

29. Composition according to any of claims 11 to 28, characterized in that it also contains an additive chosen from among an antifoam agent, a wetting agent, a surfactant and a biocide.

30. Composition according to any of claims 11 to 29, characterized in that it contains:

- 10 % to 40 % by weight of at least one particulate metal;
- 0.5 % to 10 % of a reinforcing agent for the anticorrosion properties of the composition chosen from among yttrium, zirconium, lanthanum, cerium, praseodymium and neodymium, in the form of oxides or salts, optionally associated with molybdenum oxide MoO₃;
- up to 7 % by weight of a thickener;
- 3 % to 20 % by weight of a binder;
- up to 3 % by weight, preferably between 0.05 % and 2 % by weight of a sodium and/or potassium and/or lithium silicate;
- up to 7 % by weight of one or more lubricating agents;
- 1 % to 30 % by weight of an organic solvent or a mixture of organic solvents, and
- water to make up to 100 %

31. Composition according to claim 30, characterized in that it also contains 0.1 % to 10 % by weight of a weak mineral acid such as boric acid.

32. Composition according to either of claims 30 or 31, characterized in that it also contains 0.01 % to 1 % by weight of an anionic surfactant.

33. Anticorrosion coating for metal parts, characterized in that it is obtained from a coating composition according to any of claims 11 to 31, by spraying, dip-draining or dip-centrifuging, the coating layer being subjected to a baking operation by convection or infrared for example, preferably conducted at a temperature of between 79°C and 350°C, for approximately 10 to 60 minutes, by convection.

34. Anticorrosion coating for metal parts according to claim 33, characterized in that prior to a baking operation, the coated metal parts are subjected to a drying operation, by convection or infrared for example, in particular by convection at a temperature in the region of 70°C for approximately 10 to 30 minutes on line.

35. Anticorrosion coating for metal parts according to either of claims 33 to 34, characterized in that it is applied to the metal parts to be protected with a dry film thickness of between 3 μm (11 g/m^2) and 15 μm (55 g/m^2), preferably between 4 μm (15 g/m^2) and 10 μm (40 g/m^2), further preferably between 5 μm (18 g/m^2) and 10 μm (40 g/m^2).

36. Metal substrate, preferably in steel, provided with an anticorrosion coating according to any of claims 3 to 35.

37. Substrate according to claim 36, characterized in that the anticorrosion coating is itself coated with another coating comprising an alkaline silicate, in particular a sodium and/or potassium and/or lithium silicate, an acrylic, a zirconate, a titanate, a silane, an epoxy resin, a phenol resin or one of their mixtures, these resins optionally being associated with a colloidal silica.

38. Substrate according to claim 36, characterized in that the anticorrosion coating is itself coated with another coating comprising a lubricating agent chosen from among polyethylene, polytetrafluoroethylene, MoS_2 , graphite, polysulfones, synthetic or natural waxes and nitrides and their mixtures.

INTERNATIONAL SEARCH REPORT

International Application No

IB2004/002450

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D5/08 C09D5/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 816 641 A (DACRAL SA) 17 May 2002 (2002-05-17) claims	1-38
A	DATABASE WPI Section Ch, Week 199108 Derwent Publications Ltd., London, GB; Class A21, AN 1991-055817 XP002301580 & JP 03 007785 A (TOSHIBA KK) 14 January 1991 (1991-01-14) abstract -/-	1, 4, 11, 14-18, 30, 35

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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